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SWELLING BEHAVIORS OF AMPHOTERIC POLYELECTROLYTE GELS

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The swelling behaviors of amphoteric polyelectrolyte gels, which consist of acrylic acid and allylamine hydrochloride, are studied in salt solutions. The gel reversibly swells when the concentration of NaCl is changed while the swelling of the gel becomes irreversible under the presence of $MgCl_2$. The gel swells even after the removal of $MgCl_2$ from the environmental solution These results strongly suggests that certain amount of Mg ion is trapped in the gel. A possible interaction that captures the divalent cations is the chelate formation with the carboxylic groups in the gel. The swollen gel is, thus, soaked in EDTA-2Na solution to remove Mg ions in the gel. The gel attains initial swelling ratio after soaking in the EDTA solution. The EDTA is known as a strong chelating agent that forms chelate compound with Mg ion. These results indicate that the Mg ion strongly interacts with acrylic acid in the polymer network of the gel.

Key words: gel, volume phase transition, amphoteric polyelectrolyte, chelate

1. INTRODUCTION

Gels consist of a three-dimensional polymer network that swollen in the solvent. The gel shows the volume phase transition phenomena in response to the change of environmental conditions such as temperatur, solvent composition, pH and added salt. Although many studies have been made so far, the entire aspect of the phase transition is yet to be clarified [1]. Among others, the phase transitions in the amphoteric polyelectrolyte gels are not fully studied. The details of phase transition behaviors are still controversial point and further detailed studies are required. Here, we present the phase transition behaviors of amphoteric gels consist of allylamine and acrylic acid. These monomer units are known as weak base and weak acid.

2. EXPERIMENTAL

Gels were prepared by the radical copolymerization of allylamine hydrochloride and acrylic acid at a temperature of 60°C for 12hrs. The total concentration of monomer was fixed at 3M while the ratio of each monomer unit was changed from allylamine : acrylic acid = 1 : 4 to 3 : 2. Gels thus prepared in the micropipetts of known inner diameter (141μm) were taken out of micropipetts. Then the gels were soaked in large amount of water to washed away the residual chemicals. The equilibrium diameter of gels was measured under microscope. The pH of solvent was changed. The added salt concentration in the solvent was also changed.

3. RESULTS and DISCUSSION

3.1 Hydrogen bonding effects on the swelling behaviors of gel.

Figure 1 shows the pH dependence of the equilibrium diameters of allylamine-acrylic acid gels. The gels swell both in the lower and higher pH regions while they collapse into a compact state in the intermediate pH region. The transition from the compact state to swollen state is discontinuous in the gels that contain large amount of allylamine unit. The transition, however, becomes dull as the concentration of allylamine decreases. The pH region, where the gels collapse into compact state, becomes narrower as decreasing the amount of allylamine unit.

The amphoteric polyelectrolyte gel contains both the positive and negative charges on the polymer network. The dissociation of electrolyte depends on the pH of the solvent. When the pH of the solvent decreases, the allylamine units dissociate. On the other hand, the acrylic acid units dissociate at higher pH regions. Hence, the polymer network of allylamine-acrylic acid gel contains positive or negative charges at lower or higher pH regions. The gels, therefore, swell due to the osmotic pressure that arises from the counter ion effects. The amount of net charge on the polymer network disappears at the isoelectric point. It suggests that the amphoteric polyelectrolyte gels collapses only at the isoelectric point. The experimental results obtained here, however, indicate that allylamine-acrylic acid gels collapse into compact state in certain pH regions around neutral pH. These results strongly suggest that

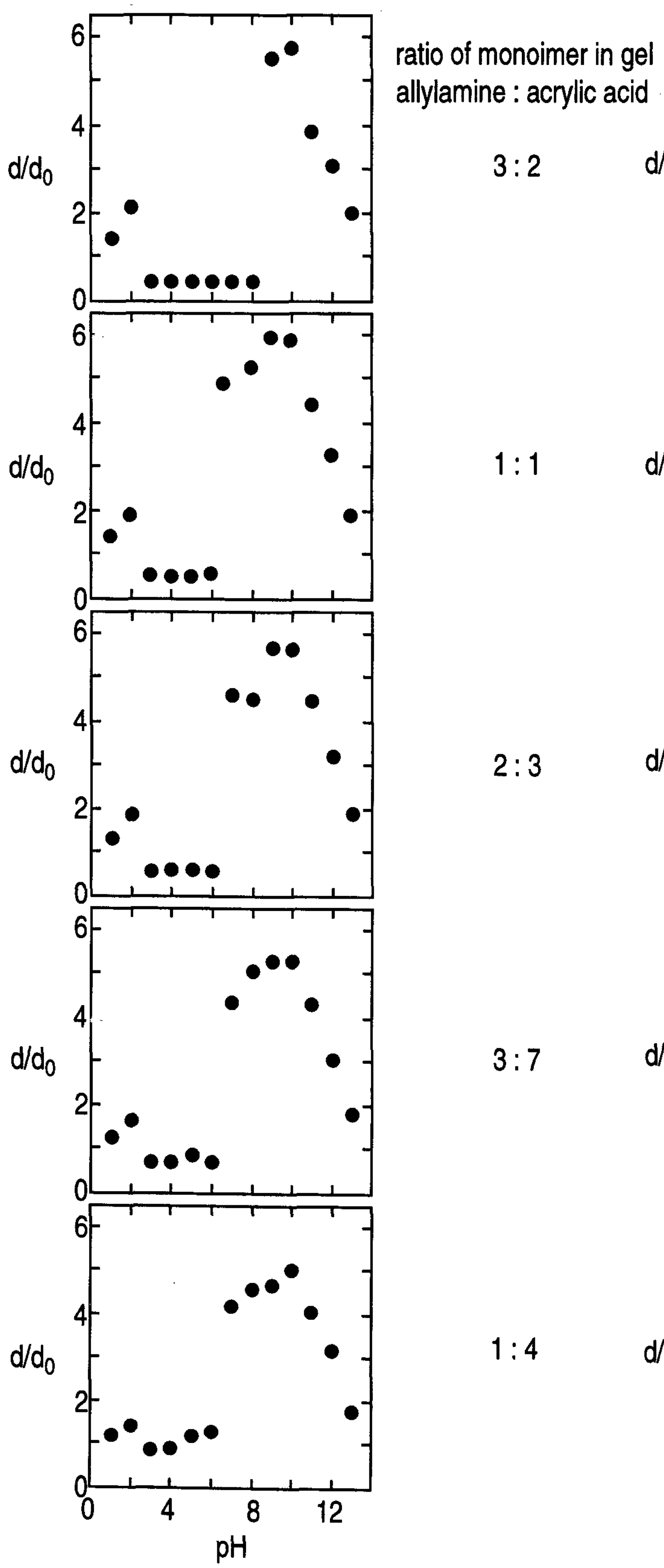

Figure 1 The pH dependence of swelling ratio d/d_0.

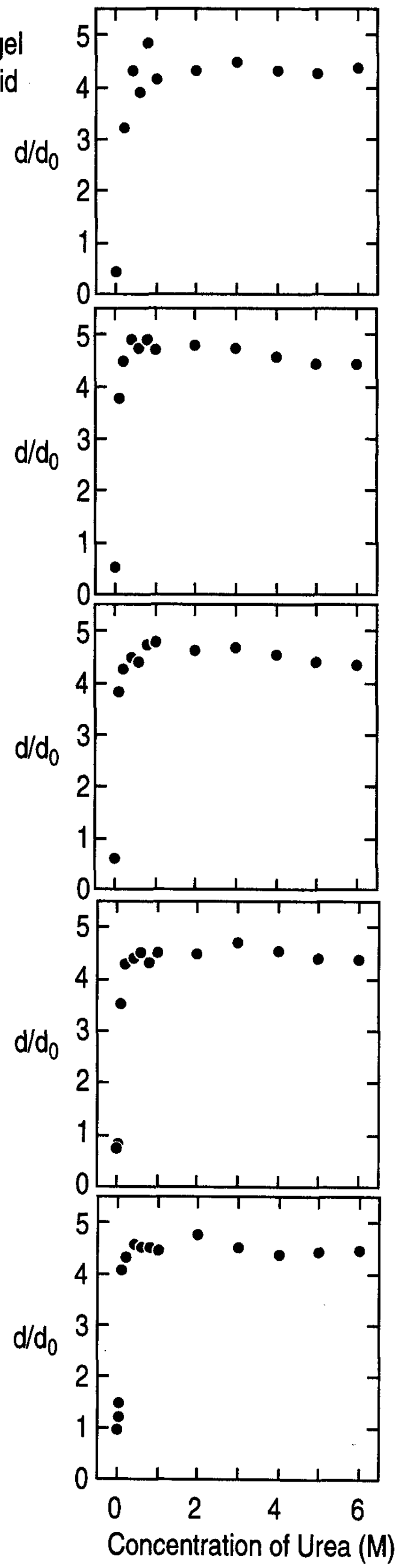

Figure 2 The dependence of swelling ratio d/d_0 on the concentration of urea.

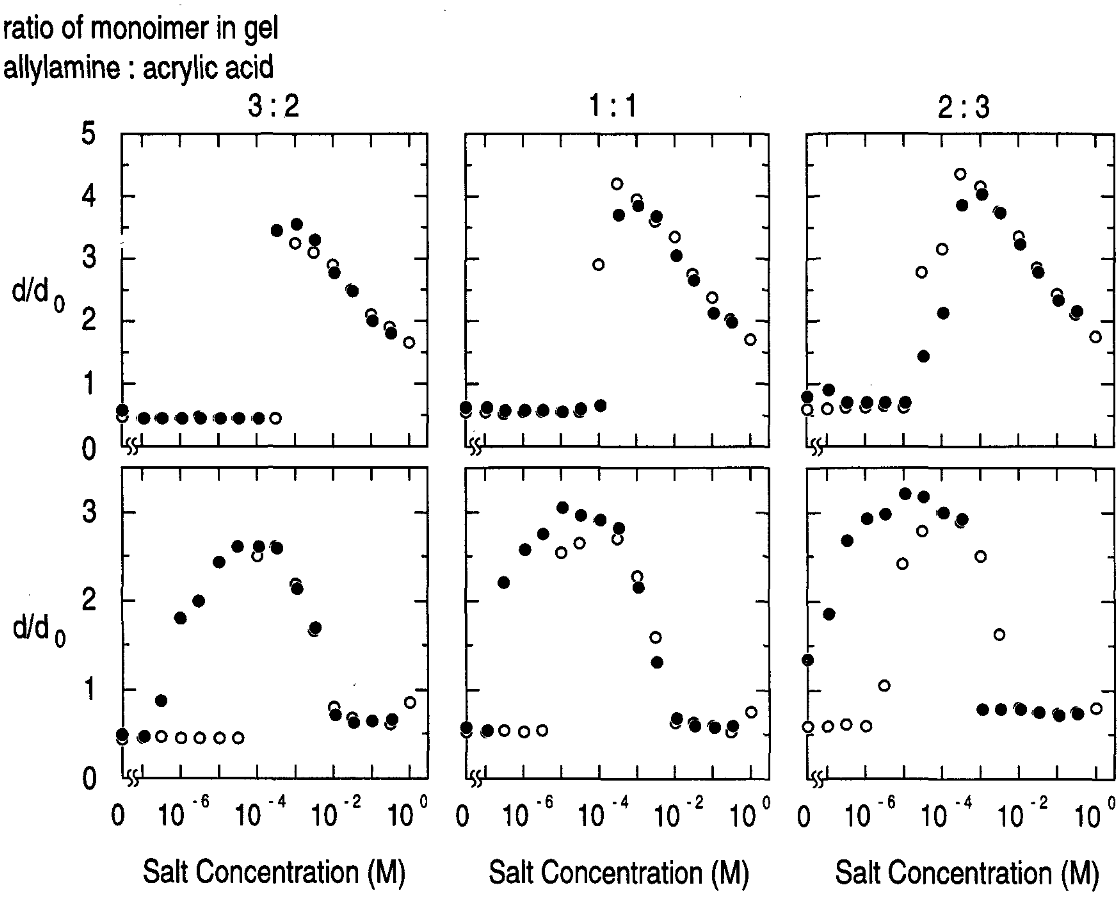

Figure 3 The swelling behaviors of gel in NaCl(upper) and $MgCl_2$(bottom) solutions. Open symbols indicate the swelling ratio of gel that measured with increasing salt concentration. Closed symbols are the swelling ratio of gel measured with decreasing salt concentration.

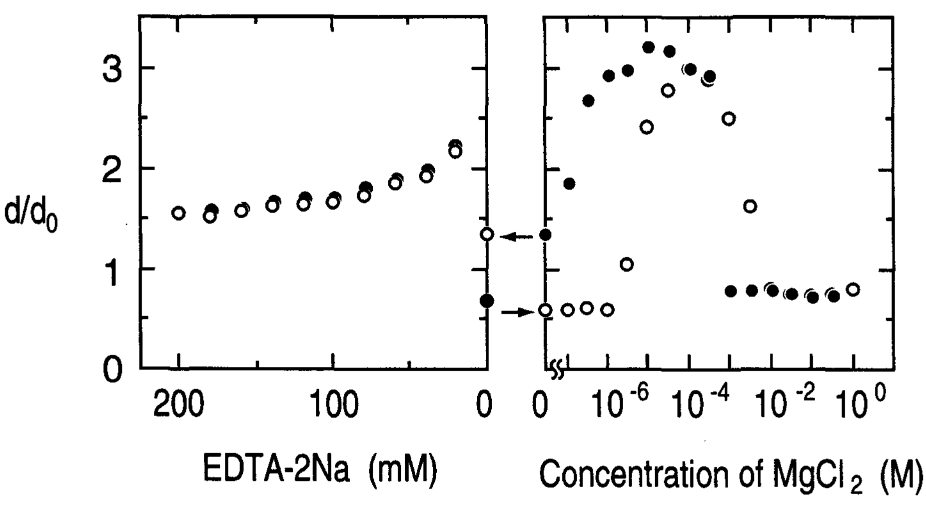

Figure 4 The swelling behaviors of gel that consists of allylamine : acrylic acid = 2 : 3. This gel shows irreversible swelling behavior in $MgCl_2$ solution (right). The gel, however, regains initial swelling ratio in water if the gel is once exposed to EDTA solution (left). Symbols are the same with Figure 3.

additional attractive interaction arise within the polymer network of the gel. The hydrogen bond is a candidate of such attractive interaction because the carboxylic group in the acrylic acid units can form the hydrogen bond [2]. The diameter of these gels is, therefore, measured as a function of urea concentration to evaluate the effects of the hydrogen bonding because urea disrupts the hydrogen bonds. The results are illustrated in Figure 2. The gels swell when soaked in urea solution. When the hydrogen bonds are disrupt, the attractive interaction between polymer chains in the gel disappears. The gel, therefore, swells in urea solution. These results indicate the formation of hydrogen bonds in the collapsed state of allylamine-acrylic acid gels.

3.2 Chlating effects on the swelling behaviors of gel.

In Figure 3, the salt concentration dependence of the radius of gel is shown. The measurements are made using single piece of gel and the salt concentration is changed. The gel swells upon increasing salt concentration while it gradually collapses at higher concentration region of salt. The swelling behaviors are reversible in the case of NaCl solution. On the other hand, the reversible transition with a large hysteresis loop is observed in the case of $MgCl_2$ at lower concentrations of acrylic acid unit in the gel. When the amount of acrylic acid unit in the gel exceeds 50%, the swelling behaviors become irreversible. In these gels, gels are still swollen in water after a cyclic change of salt concentration.

The swelling behaviors of the gels in NaCl solution are similar to that of simple polyelectrolyte gel in which the counter ion effects play essential roles [3]. The irreversible swelling behaviors of the gels in $MgCl_2$ solution, however, suggest the presence of repulsive interactions in the polymer network of gel after a cyclic change of salt concentration. Since the gels are initially in the compact state, the hydrogen bonds are formed in the polymer network of the gel. It may be natural to expect that the interaction between Mg ion and either monomer units prevent the formation of hydrogen bond after cyclic change of $MgCl_2$ concentration. The carboxyl group in acrylic acid monomer unit is known to form chelate with divalent cations such as Mg, Mn, and Ca [4]. Hence, if the chelate structure is disrupt, the volume phase transition becomes reversible. The gels, that are swollen in water after a cyclic change of salt concentration, are washed by EDTA solution that is known as a strong chelating agent of divalent cations. Figure 4 shows the swelling curves of the gel in EDTA solution. The gels once swell in EDTA solution when the concentration of EDTA is increased. The swelling curve of gel follow the same path in the decreasing process of EDTA concentration. Finally the gels regain the initial collapsed state in water. These results strongly suggest the formation of chelate structure in allylamine-acrylic acid gels.

4. CONCLUSIONS

The swelling behaviors of amphoteric gels, which consist of allylamine and acrylic acid, are studied under various experimental conditions such as pH and salt concentration. It is found from the pH dependence of the swelling ratio that the gels swell both lower and higher pH regions due to the dissociation of each monomer unit. This swelling behavior is a characteristic of amphoteric polyelectrolyte gels. The gels, however, shrink into a compact state in the pH region around neutral pH. These results suggest the existence of attractive interaction within the gel. This swelling behavior of allylamine-acrylic acid gels cannot be explained by the simple electrolyte effects. The swelling behaviors of gels in urea solution strongly suggest the formation of hydrogen bond in the gel. The attractive interaction due to the hydrogen bonding, therefore, collapses allylamine-acrylic acid gels into a compact state in the neutral pH region. The results further suggest that the hydrogen bonds are formed in the gel spontaneously.

The reentrant volume phase transition of allylamine-acrylic acid gel is observed in the salt solution. The transition is entirely reversible in NaCl solution. The volume phase transition, however, becomes irreversible in $MgCl_2$ solution. The irreversible phase transition can be explained in terms of the chelate formation between Mg ion and carboxyl groups of acrylic acid units. These results indicate that allylamine-acrylic acid gel captures the divalent cations. It further suggests that the gel can sense Mg ions in the environment.

5. REFERENCES

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